

Determining the Solubility Product Constant of Calcium Hydroxide

PURPOSE

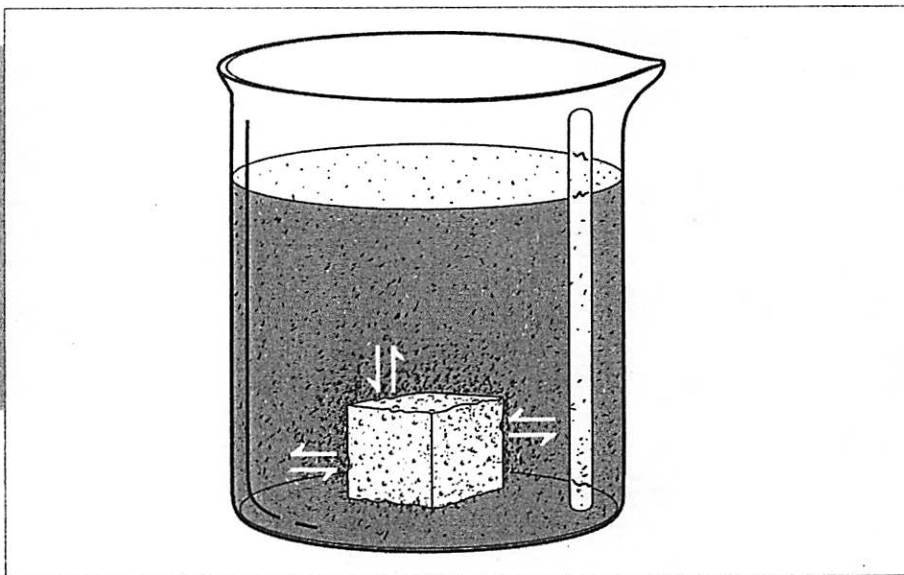
- Determine the solubility product constant (K_{sp}) of $\text{Ca}(\text{OH})_2$ by various methods, including measuring the dry mass and recording the pH of a saturated solution
- Determine the solubility product constant of $\text{Ca}(\text{OH})_2$ by titrating a saturated solution with HCl, finding the equivalence point of titration, and calculating molar solubility
- Compare the three laboratory methods for precision and analyze possible sources of error

INTRODUCTION

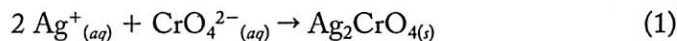
The **solubility** of a compound in water may be considered the maximum amount of solute that dissolves in a given amount of water at specified temperature and pressure. When the maximum amount of solute has dissolved, the resulting solution is called a **saturated solution**. If more solute is added, it will not dissolve but rather remain solid. At this point, an equilibrium between the aqueous and solid solute, called **solubility equilibrium**, may be achieved.

Figure 18.1

Because of a dynamic equilibrium between the solid and its ions, any addition of solute to this saturated solution will only contribute to the amount of solid.



Although a solute may be a molecular compound, most solubility equilibria investigated in chemistry involve ionic compounds. In investigating the solubility of ionic compounds, it is helpful to adopt a change in mindset that is opposite to the way we study solubility in precipitation reactions, where the solid is a *product*, as in this example:



By contrast, solubility equilibrium reactions for ionic compounds are written for the *solid reactant* that is dissolving in water and dissociating into ions. The solubility for the silver chromate precipitate formed in reaction (1) would be written as



The equilibrium constant for solubility equilibria is called the **solubility product constant**, or K_{sp} . The K_{sp} expression for reaction (2) is $K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$. The solid is not included in such an expression, because its ionic concentrations do not change, no matter how much solid is present.

Investigating reaction (2) further, one can find that $K_{sp} = 1.2 \times 10^{-12}$ at 25°C. However, note well: this value does not help you determine the concentration of silver chromate that actually dissolved in the solution to make it saturated; for this one must calculate the molar solubility of silver chromate. A saturated solution must be made before a precipitate forms. In “equilibrium speak,” the reaction quotient, Q , must be greater than K_{sp} to have a precipitate form. Working backwards, it is relatively straightforward to calculate the molar solubility and the concentration of all ions at 25°C, in the following manner:

Let $x = [\text{CrO}_4^{2-}]_{Eq}$. Then

	$\text{Ag}_2\text{CrO}_{4(s)} \rightleftharpoons 2 \text{Ag}^+_{(aq)} + \text{CrO}_4^{2-}_{(aq)}$	
Initial (M)	-----	0 0
Change {Δ} (M)	-----	+2x +x
Equilibrium (M)	-----	2x x

$$\text{Because } K_{sp} = [2x]^2 [x] = 1.2 \times 10^{-12}$$

$$4x^3 = 1.2 \times 10^{-12}$$

$$\text{and } x = 6.7 \times 10^{-5} \text{ M} = [\text{CrO}_4^{2-}]_{Eq}$$

By substituting this value of x into the table above, we then find that

$$[\text{Ag}^+] = 2x = 1.3 \times 10^{-4} \text{ M}$$

The value of x also represents the molar solubility of silver chromate. Solubility is sometimes represented as mass of solute/volume of solution. Conversions between this form of solubility and molar solubility require molar mass conversions and volume conversions. For example, the solubility of silver chromate in g solute/1.00 L solution is

$$\frac{6.7 \times 10^{-5} \text{ moles Ag}_2\text{CrO}_4}{1.00 \text{ L}} \times \frac{331.74 \text{ g Ag}_2\text{CrO}_4}{1 \text{ mole Ag}_2\text{CrO}_4} = \frac{2.22 \times 10^{-2} \text{ g Ag}_2\text{CrO}_4}{1.00 \text{ L}}$$

In order to measure a solubility product equilibrium constant, one must have a saturated solution. Then, by determining the concentration of one ion in the saturated solution and using stoichiometry, the K_{sp} can be calculated.

Procedure Preview The solubility product constant, K_{sp} , for calcium hydroxide will be determined by different methods and the results compared to find the best method for determining this K_{sp} . In the first method, a known volume of a saturated solution of $\text{Ca}(\text{OH})_2$ is put in a dried beaker, the mass of which has been measured, and the water driven off in an oven. The mass of the solid $\text{Ca}(\text{OH})_2$ is then measured to determine K_{sp} . The second method employs a calibrated pH probe to measure the pH of the saturated solution of $\text{Ca}(\text{OH})_2$. The $[\text{OH}^-]$ is determined and used to calculate K_{sp} . In a third approach, the saturated $\text{Ca}(\text{OH})_2$ solution is titrated with HCl. The resulting titration curve is used to determine the equivalence point of the titration, and then K_{sp} is determined using the molar solubility of $\text{Ca}(\text{OH})_2$. As a variation on Method 3, your instructor may direct you to follow Method 4, a microscale titration of saturated $\text{Ca}(\text{OH})_2$ solution using various indicators.

Pre-Lab Questions

1. Taking the K_{sp} for $\text{Ca}(\text{OH})_2$ from your textbook, calculate
 - a. its molar solubility
 - b. its solubility in g/100 mL
2. Calculate the theoretical volume of 0.020 M HCl that must be added to 25.00 mL of saturated calcium hydroxide, in order to reach the equivalence point of the titration.
3. Predict the pH at the equivalence point of the titration of $\text{Ca}(\text{OH})_2$ with HCl, explaining your reasoning thoroughly.

Method 1: Drying

MATERIALS

- tongs
- pipet bulb
- balance
- saturated solution of $\text{Ca}(\text{OH})_2$
- 50-mL beaker
- 25-mL volumetric pipet (or other volume-measuring device)
- drying oven (*alternatives*: hot plate; or Bunsen burner with ring, ring stand, and wire square)

PROCEDURE

- Step A** Use tongs to manipulate the beaker throughout this procedure.
- Step B** Place the 50-mL beaker in drying oven, allowing it to dry completely.
- Step C** Measure the mass of the beaker.
- Step D** Using a volumetric pipet, add 25.00 mL of saturated calcium hydroxide solution to the beaker and place in drying oven.
- Step E** Let beaker with $\text{Ca}(\text{OH})_2$ solution dry completely, then remove from oven. Let cool.
- Step F** Measure mass of beaker and solid calcium hydroxide.
- Step G** Return beaker to oven, allowing to dry longer. Mass again after cooling to ensure that all water evaporated. If mass decreases, repeat drying until there is no major mass change.

Method 2: Initial pH

Note: This section may be skipped if you are conducting Method 3, because the initial pH determined in Step G of Method 3 provides the data needed to make the calculation of K_{sp} .

MATERIALS

- pH meter
- saturated $\text{Ca}(\text{OH})_2$ solution
- 50-mL beaker
- pH standards (pH=4.00 and pH=10.00)
- distilled water (in squirt bottle)
- magnetic stirrer
- microstir bar

PROCEDURE

- Step A** Calibrate the pH meter according to your instructor's directions.
- Step B** Rinse pH meter tip with distilled water and pat dry with paper towel.
- Step C** Pour some saturated $\text{Ca}(\text{OH})_2$ into the beaker, adding enough to cover bulb of pH meter.
- Step D** Allow pH reading to stabilize while solution is being stirred (either manually or using the stir bar and magnetic stirrer). Record the pH of this solution.

Method 4: Microscale Titration

MATERIALS

- saturated $\text{Ca}(\text{OH})_2$ solution
- 0.020 M HCl solution (standardized)
- 24-well microplate
- microstir bars (3)
- magnetic stirrer
- 1.0-mL volumetric pipet
- micropipet
- bromophenol blue
- phenolphthalein
- bromocresol green

PROCEDURE

- Step A** Measure 0.80 mL of saturated $\text{Ca}(\text{OH})_2$ solution into each of 3 microwells and place a microstir bar in each well.
- Step B** Add 1 drop of each indicator in a separate well of saturated $\text{Ca}(\text{OH})_2$ solution.
- Step C** Place a sheet of white paper on the stir plate, then place the microwell plate on the magnetic stirrer with the appropriate well on the center of the stir plate. Turn on the stir plate. Prepare buret by rinsing it with 0.020 M HCl, removing any air bubbles from tip.
- Step D** Fill buret to the 0.000-mL mark.
- Step E** Titrate until appropriate color change is permanent. You must be patient close to endpoint, because it takes a few seconds for complete mixing of solution and color change of the indicator.
- Step F** Recenter the plate on the next well containing saturated $\text{Ca}(\text{OH})_2$, and titrate this sample.
- Step G** Repeat Step F for third and final sample.

Calculations

In your lab report, include your computations and conclusions for the following questions.

1. Write a balanced chemical equation that describes the solubility of calcium hydroxide and write the K_{sp} expression for it.
2. Find the theoretical K_{sp} value, citing your source.
3. Calculate the K_{sp} of calcium hydroxide for *each* of the lab methods followed. Show *all* work in each case.

Method 1: Find the molar solubility of $\text{Ca}(\text{OH})_2$ and use this to calculate K_{sp} .

Method 2: Use the $[\text{OH}^-]$ from the initial pH (before HCl is added) to calculate K_{sp} .

Method 3: Graph the titration curve of pH versus volume (mL) of 0.020 M HCl added. On the titration curve, determine volume (to appropriate significant figures) of HCl added to reach the endpoint at $\text{pH} = 7.00$. With this volume, determine the concentration of $\text{Ca}(\text{OH})_2$ in the saturated solution, and then calculate K_{sp} .

Method 4: Use stoichiometry to calculate molarity of $\text{Ca}(\text{OH})_2$ and then K_{sp} .

Post-Lab Questions

1. What K_{sp} do you get from Method 1?
2. What K_{sp} do you get from Method 2?
3. Using the initial pH reading from Step G of Method 3, calculate the K_{sp} of $\text{Ca}(\text{OH})_2$.
4. Is the experimentally determined pH at the equivalence point of the titration in Method 3 consistent with the theoretical value? If not, cite one possible error source that would lead to your actual experimental value. Explain thoroughly.
5. Which method is the most accurate? Explain your answer completely, giving examples of possible error sources in each case.
6. When a saturated solution of $\text{Ca}(\text{OH})_2$ is stored, why is it best to be sure that some solid is present?
7. What would happen to the calculated value for the K_{sp} of $\text{Ca}(\text{OH})_2$ if there were an air bubble in the buret tip when you started the titration, and this air bubble were drained during the titration? Explain your reasoning in detail.
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 - a. Suppose that the saturated solution of $\text{Ca}(\text{OH})_2$ were stored in an open container at constant temperature and half of the water evaporated. What would happen to the calculated K_{sp} value? Explain.
 - b. What changes would you observe in the storage bottle after the water evaporated?
9. Many orange juices that are fortified with calcium contain a mixture of calcium hydroxide/citric acid/maleic acid. How does mixing the calcium hydroxide with these acids increase the molar solubility of $\text{Ca}(\text{OH})_2$? Explain in detail, including balanced chemical reaction equations to support your explanation.
10. Compare your results for the microscale titration for each indicator. Should all of these indicators result in the same K_{sp} value? Why or why not? Be sure to include a theoretical titration curve as part of your answer.